



## Atomistic Picture of Platinum Structural Changes During Electrocatalysis and Mitigation Strategies for Long Term Stability

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### ► To cite this version:

Jakub Drnec, Martin Ruge, Timo Fuchs, Raphaël Chattot, Isaac Martens, et al.. Atomistic Picture of Platinum Structural Changes During Electrocatalysis and Mitigation Strategies for Long Term Stability. 25th Topical Meeting of the International Society of Electrochemistry, May 2019, Tolède, Spain. hal-02471956

**HAL Id: hal-02471956**

**<https://hal.science/hal-02471956>**

Submitted on 10 Feb 2020

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# Atomistic Picture of Platinum Structural Changes During Electrocatalysis and Mitigation Strategies for Long Term Stability.

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The durability of an electro-active material (e.g. Pt catalyst in proton exchange membrane fuel cells (PEMFC)) is a major barrier, preventing faster commercialization of energy conversion and storage devices for stationary and transportation applications. In the case of PEMFC, the decrease in performance is partially due to irreversible processes in the catalyst layers, such as dissolution and morphology changes of Pt nanostructures. Even though these processes have been extensively studied in the past, there are still many important questions unanswered related to the actual degradation mechanisms [1 and references there-in]. Therefore further fundamental understanding of the Pt oxidation, reduction, dissolution, and restructuring mechanisms, together with their atomistic picture, is clearly needed in order to incorporate the state-of-the-art catalysts into the PEMFC device and make the technology more commercially competitive.

I will discuss the results of in-situ and operando structural X-ray studies performed on various Pt single crystal surfaces (Pt(111), Pt(100)) and on nanoparticle catalysts (NP) during the electrochemical oxide formation and its reduction [2-8]. We use advanced synchrotron based diffraction techniques to gain a detailed atomistic picture of the place-exchange (PE), dissolution and restructuring taking place in idealized conditions of the half cells and in PEMFC during operation.

Severe surface reorganization due to the PE process occurs in the potential range relevant to the ORR. Interestingly, the exact position of the PE atom on the surface is the decisive factor which determines the extent of surface restructuring and dissolution. If the PE atom is positioned exactly above its vacancy (e.g. on Pt(111) at low potentials), the PE process is reversible. However, if the PE atom moves laterally from its vacancy, the diffusion barrier prevents the diffusion back to the vacancy and the surface restructures and dissolves in the reduction step. The surface orientation, potential, and time play a decisive role in this process. The PE and surface restructuring have severe consequences as they cause activity loss of the state-of-the-art shaped NP catalysts (octahedra, cubes) in accelerated stress tests and they are also responsible for the poor stability of core-shell nanostructures. It is also one of the main reasons why the incorporation of advanced Pt based catalysts into the next generation PEMFCs remains a challenging task.

Yet nothing is lost and possible knowledge based mitigation strategies, involving additives, particular core-shell structures and defects engineering, can be developed. For example, a new class of defectious Pt catalysts show extraordinary stability, as the reorganization does not significantly alter the morphology which is solely responsible for the high activity [9]. In these materials the defects are used to tune the electronic structure, instead of more traditional approaches such as alloying or shape engineering.

## References:

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